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Photoconductivity measurements on stable photocrosslinkable nonlinear optical polymer - PVCN (polyvinylcinnamate)/CNNB-R (3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene) are reported. Photoconductivity in this polymer system, in both crosslinked and uncrosslinked states, was observed without introducing any sensitizer or carrier-transport agents. Absorption of CNNB-R (λpeak = 518 nm) results in photocarrier generation and it is conjectured that CNNB-R also plays a role in the carrier transport. Such polymers are candidate materials for photorefraction.

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Photoconductivity in a Photocrosslinkable Second-Order Nonlinear Optical Polymer

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Abstract. Photoconductivity measurements on a stable photocrosslinkable nonlinear optical polymer – PVCN (polyvinylcinnamate)/CNNB-R (3-cinnamoyloxy-4-[4-N,N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene) are reported. Photoconductivity in this polymer system, in both crosslinked and uncrosslinked states, was observed without introducing any sensitizer or carrier-transport agents. Absorption of CNNB-R (λ_{peak} = 518 nm) results in photocarrier generation and it is conjectured that CNNB-R also plays a role in the carrier transport. Such polymers are candidate materials for photorefraction.

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Photorefractive effect in various inorganic crystals have been extensively investigated for many years [1]. Photorefractive materials have interesting potential applications, such as real-time holography, optical data storage, image processing and optical switching. Recently, Sutter et al. [2] observed the photorefractive effect in an organic crystal – COANP doped with TCNQ. The organic crystals possess large electro-optic coefficients and can lead to enhanced light induced diffraction efficiencies. However, growth and polishing of the soft organic crystal are difficult tasks. More recently, photoconduction has been observed in nonlinear optical polymers [3, 4]. These polymeric materials provide another path to achieve sensitive photorefractive media. Nonlinear optical polymers not only possess large electro-optic coefficients and low dielectric constants, but their optical properties can also be easily tailored by either doping or covalently incorporating different functional groups into the polymer. This can give rise to both nonlinearity and photoconductivity in the polymer. Such polymeric photorefractive media would be particularly attractive for waveguide applications.

The requirements for a material to exhibit the photorefractive effect are photocarrier generation and charge transport, low dark conductivity, and electro-optic properties. Schildkraut [3] recently reported on a photoconductive electro-optic polymer, in which photoconductivity was introduced by adding perylene photosensitizer and triarylamine hole transport molecules to a nonlinear optical polymer. The host polymer contained a stilbene chromophore as nonlinear optical side chain. The photorefractive figure of merit was also calculated to be 2.45 pm/V for this material. More recently, Ducharme et al. [4] observed the photorefractive effect in the nonlinear optical polymer composed of bis-phenol-A-diglycidyl-ether reacted with the nonlinear chromophore 4-nitro-1,2-phenylenediamine (NPDA). The photocarrier generation in this material originated from the nonlinear optical chromophore (NPDA), but the photocarrier transport was achieved by the addition of a hole transport agent – diethylamino-benzaldehyde–diphenylhydrazone (DEH). By application of external fields of the order of 100 kV/cm, they measured diffraction efficiencies of the order of 10^{-5}. In these polymer systems, the addition of sensitizers and charge transport agents limit the density of nonlinear optical chromophore, thereby considerably reducing the electro-optic coefficient and the diffraction efficiency. Additional problems arise due to phase segregation [4] of the hole transport agent in the polymer. Such effects can cause undesirable light scattering from the photorefractive medium and also limit the lifetime of the materials.

Addition of sensitizers and charge transport agents to a thermally crosslinkable nonlinear optical polymer creates further difficulties in achieving stable nonlinearities. The plasticization due to these additives may lower the glass transition temperature as well. Ideally the nonlinear optical chromophores, sensitizers and charge transport agents should all be functionalized into a polymeric network architecture. In this paper we report photocon-

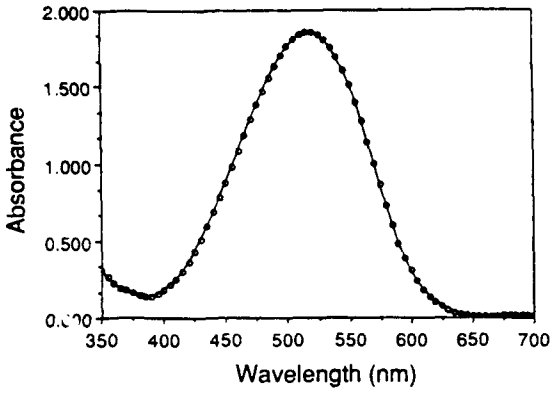

Fig. 1. Optical absorption spectrum of the polymer film

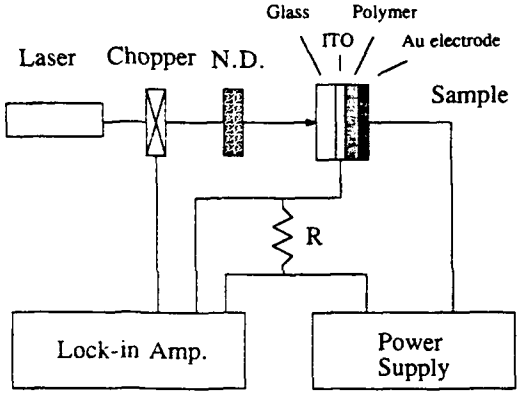

Fig. 2. Experimental set-up for photoconductivity measurement

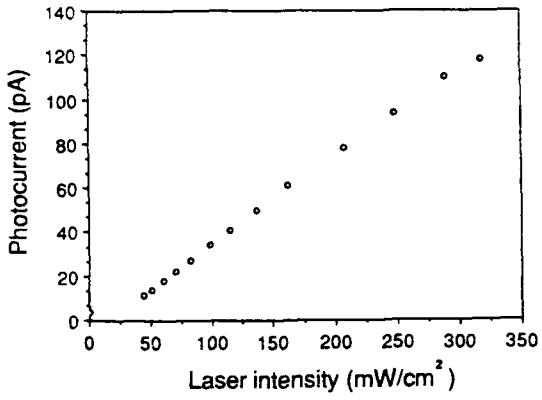

Fig. 3. Photocurrent measured as a function of laser intensity at 514 nm with 10 V bias

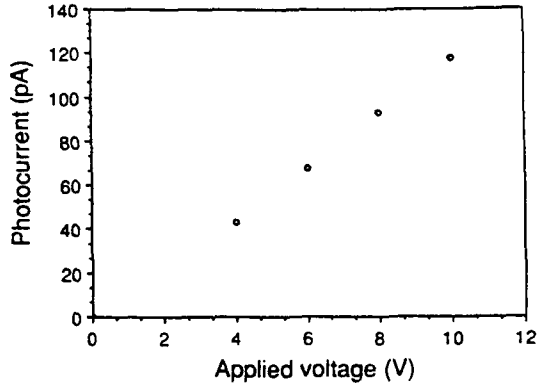

Fig. 4. Photocurrent measured as a function of bias voltage at 514 nm with laser intensity of 0.3 W/cm²

ductivity measurements in a photocrosslinkable, stable, nonlinear optical polymer without any doping with sensitizers and charge transport agents.

A photocrosslinkable nonlinear optical polymer – PVCN (polyvinylcinnamate)/CNNB-R (3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene) was used in this study. No additional hole transport agent was incorporated into this polymer system. This polymer system exhibits large and stable second order nonlinear optical coefficients [5, 6]. The chemical structure of this guest (CNNB-R) and host (PVCN) polymer was reported in [5]. For the photoconductivity measurements, a polymer film with 28.6 wt.% nonlinear optical chromophore was spin-coated on an ITO (indium-tin-oxide) covered glass slide where the transparent ITO coating serves as an electrode. This nonlinear optical polymer guest host system is completely compatible and does not phase segregate even at extremely high dye concentrations [7]. A gold layer of 500 Å thickness was thermally evaporated onto the polymer film to form the second electrode. The thickness of the polymer film was measured to be 1.25 μm with an ellipsometer. The optical absorption spectrum of the sample is shown in Fig. 1. The absorption peak at 518 nm is due to CNNB-R chromophores. Samples where the nonlinear optical units were crosslinked into the polymeric host were photocrosslinked before evaporating the gold electrodes.

The experimental set-up for the photoconductivity measurement is schematically shown in Fig. 2. An Ar^+ laser beam illuminates the biased polymer film through an ITO coated glass slide after passing through a mechanical optical chopper and an adjustable neutral density filter. The photocurrent generated by the incoming photons results in a voltage drop across a 1 MΩ resistor. This voltage is measured with a lock-in amplifier. Photoconductivity of the polymer films was studied at various laser intensities, bias voltages and different laser wavelengths.

The measured photocurrents were approximately linear with the laser intensity and the bias voltage as shown in Figs. 3 and 4. With 0.3 W/cm² incident radiation at 514 nm and 10 V bias, the photoconductivity was calculated to be $\sigma_{pc} = 4.7 \times 10^{-14}\,\Omega^{-1}\,cm^{-1}$ and the photosensitivity was extracted as $\sigma_{pc}/I = 1.5 \times 10^{-13}\,\Omega^{-1}\,cm^{-1}/(W/cm^2)$. This value is of the same order of magnitude as that reported in the hole-transport agent doped polymer [4]. The photocurrent was found to be insensitive to temperature for $T < T_g$. The T_g for this material is 80° C and the conductivity measurements were carried out btween 20 to 50° C.

The measured photocurrent as a function of laser wavelength at a fixed value of laser intensity and bias voltage is shown in Fig. 5. The spectral dependence of the photocurrent shows a similar behavior to the measured optical absorption in this polymer film. This sug-

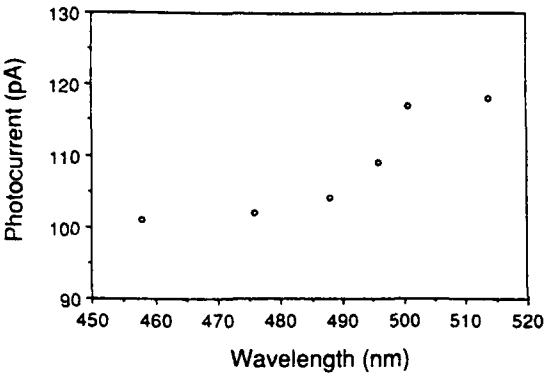

Fig. 5. Photocurrent measured as a function of laser wavelength at 10 V bias with laser intensity of 0.3 W/cm^2

gests that optical excitation of CNNB-R chromophores is the origin of photocarrier generation. This result is similar to the behavior of the nonlinear optical polymer in [4]. The measured photocurrent in our polymer system seems to indicate that the nonlinear optical chromophore CNNB-R also plays the role of a charge transporter, making it unnecessary to introduce an external agent. Photoconductivity in both photocrosslinked and uncrosslinked systems was found to be the same within the limits of experimental error. In the photocrosslinked system the cinnamoyl groups from the host polymer and the guest nonlinear optical unit are depleted as a result of photocrosslinking. The donor group in the CNNB-R system is expected to form a stable hole and is conjectured to participate in the charge transport process as well. The photorefractive diffraction efficiency figure of merit [3] $Q = n^3 r/\varepsilon$ was estimated to be 12 pm/V in our polymer, where n is the refractive index, r is the electro-optic coefficient and ε is the dielectric constant.

In conclusion, we have measured the photocurrent in a photocrosslinkable nonlinear optical polymer as a function of laser wavelength, intensity and applied field. For both the uncrosslinked and stable nonlinear optical photocrosslinked systems similar photocurrent behavior was observed. The photoconductivity and photosensitivity have been calculated. The polymers require no additional charge transporting agents to facilitate photoconduction. The photoconductivity of these polymer films are stable at room temperature over a period greater than two months. We continue to monitor the photocurrent stability in this polymer system. Experiments on the measurements of photorefractive diffraction efficiency in this material are currently underway.

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